

THEORETICAL INVESTIGATION OF FULLERENE NANOCAGE CAPACITY  
FOR HYDROGEN STORAGE

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*Dedicated to my beloved family*

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## ABSTRACT

Fullerenes are nanocage compounds that can be used for hydrogen storage. Hydrogen is believed to be a potential alternative energy source, as the energy produced is clean. One of the most important issues in hydrogen-filled fullerene molecules is the determination of the number of hydrogen molecules that can be encapsulated inside the fullerene cage. In this study, the maximum number of hydrogen molecules that can be encapsulated inside  $C_{50}$ ,  $C_{60}$ ,  $C_{70}$  and  $C_{78}$  fullerenes was investigated by means of theoretical methods. Various density functional theory (DFT) functionals, together with Hartree–Fock (HF) and post Hartree–Fock methods were used in the computation for this study. Taking into consideration the basis set superposition error (BSSE) correction, it was found that second order Møller–Plesset perturbation theory (MP2) and dispersion corrected semiempirical hybrid density functional theory with perturbative second-order correlation (B2PLYPD), in conjunction with the triple zeta Pople-style 6–311G(d,p) basis set, provide the most reliable results in predicting the stability of  $nH_2@C_k$  complexes. On the basis of complexation energy calculations, it was confirmed that encapsulation of numerous hydrogen molecules inside  $C_k$  ( $k = 50, 60, 70$  and  $78$ ) fullerenes is unrealistic. In agreement with results of experimental works, only one hydrogen molecule can be accommodated inside  $C_{50}$  and  $C_{60}$ , two inside  $C_{70}$  and three inside  $C_{78}$ . Geometrical considerations of encapsulation of  $H_2$  molecule(s), host–guest interaction forces, strain energies, dispersion energies, maximum expansion of the fullerene cages that can be reached before breaking some of the C–C bonds and the bond dissociation energies (BDEs) of the cages are all in line with the calculated complexation energies.

## ABSTRAK

Fulerena adalah sebatian sangkar bersaiz nano yang boleh digunakan dalam penyimpanan hidrogen. Hidrogen dipercayai mempunyai potensi untuk menjadi sumber tenaga alternatif kerana tenaga yang dijana daripadanya adalah bersih. Salah satu isu penting dalam fulerena berisi dengan molekul hidrogen adalah penentuan bilangan molekul hidrogen yang boleh terkandung dalam memenuhi ruang sangkar fulerena tersebut. Dalam kajian ini, bilangan maksimum molekul hidrogen yang boleh terkandung di dalam fulerena  $C_{50}$ ,  $C_{60}$ ,  $C_{70}$  dan  $C_{78}$  telah dikaji melalui kaedah teori. Pelbagai fungsi teori fungsi ketumpatan (DFT), bersama-sama dengan kaedah teori Hartree-Fock (HF) dan pasca Hartree-Fock telah digunakan dalam pengiraan untuk kajian ini. Dengan mengambil kira pembetulan set asas ralat tindihan (BSSE), ianya didapati bahawa teori gangguan Møller-Plesset tertib kedua (MP2) dan teori hibrid separa empirikal fungsi ketumpatan penyerakan diperbetulkan dengan korelasi gangguan tertib kedua (B2PLYPD), bersama dengan set asas zeta tiga kali ganda jenis Pople 6-311G(d,p), memberikan keputusan yang paling sesuai dalam meramal kestabilan kompleks  $nH_2@C_k$ . Pengiraan tenaga pengkompleksan mengesahkan bahawa pengkapsulan molekul hidrogen yang banyak di dalam fulerena  $C_k$  ( $k = 50, 60, 70$  dan  $78$ ) adalah tidak realistik. Hasil eksperimen bersetuju hanya satu molekul hidrogen boleh terkandung di dalam  $C_{50}$  dan  $C_{60}$ , dua di dalam  $C_{70}$  dan tiga di dalam  $C_{78}$ . Pertimbangan geometri dalam pengkapsulan molekul  $H_2$ , kuasa-kuasa interaksi perumah-tetamu, daya, tenaga terikan, tenaga penyerakan, pengembangan maksimum dalam interaksi yang berlaku di dalam sangkar fulerena yang boleh dicapai sebelum memecah beberapa ikatan C-C dan tenaga penceraian ikatan (BDEs) di dalam sangkar. Semuanya adalah selaras dengan tenaga pengkompleksan yang dikira.

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## LIST OF ABBREVIATIONS

SWCNTs	-	Single-Walled Carbon Nanotubes
MWCNTs	-	Multi-Walled Carbon Nanotubes
M	-	Metal
MF	-	Metal-Containing Fullerene
EMFs	-	Endohedral Metallofullerenes
NMR	-	Nuclear Magnetic Resonance Spectroscopy
EPR	-	Electron Paramagnetic Resonance
XAFS	-	Extended X-Ray Absorption Fine Structure
IR	-	Infrared Spectroscopy
Raman	-	Raman Spectroscopy
DMA	-	9,10-Dimethylantracene
MM	-	Molecular Mechanics
CFF	-	Consistent Force Field
ESFF	-	Extensible Systematic Force Field
CFF	-	Constrained Force Fields
CVFF	-	Consistent-Valence Force field
EFF	-	Empirical Force Fields
AMBER	-	Assisted Model Building With Energy Refinement
CHARMM	-	Chemistry At Harvard Macromolecular Mechanics
GROMOS	-	Molecular Dynamics Simulation Developed at the University of Groningen

AM1	-	Austin Model 1
PM3	-	Parameterized Model Number 3
MNDO	-	Modified Neglect of Differential Overlap
MO	-	Molecular Orbital
STO's	-	Slater Type Orbitals
GTOs	-	Gaussian Type Orbitals
LCAO–MO	-	Linear Combination of Atomic Orbitals–Molecular Orbitals
SV	-	Split Valence
HF	-	Hartree–Fock
SCF	-	Self–Consistent Field
Post–SCF	-	Post–Hartree–Fock
EC	-	Electron Correlation
MP <sub>n</sub>	-	Møller Plesset Perturbation Theory at the n <sup>th</sup> Order
MP2	-	Second–Order Møller–Plesset Perturbation Theory
SCS–MP2	-	Spin–Component Scaled MP2
SAPT	-	Symmetry–Adapted Perturbation Theory
MP4	-	Fourth–Order Møller–Plesset Perturbation Theory
QCI	-	Quadratic Configuration Interaction Methods
CISD	-	Single and Double Excitation CI Methods
QCISD	-	Quadratic CI with Single and Double Excitation
CC	-	Coupled Cluster Methods
DFT	-	Density–Functional Theory
LDA	-	Local Density Approximation
LSDA	-	Local Spin Density Approximation
B	-	Becke88
PW91	-	Perdew–Wang 91

MPW	-	Modified Perdew–Wang by Barone and Adamo
G96	-	Gill96
LYP	-	LYP by Lee, Yang, and Parr
B3LYP	-	Becke, 3–Parameter, Lee–Yang–Parr
BHandHLYP	-	Becke–Half–and–Half–LYP (Lee–Yang–Parr)
MPWB1K	-	Modified Perdew–Wang, Becke Functional
SVWN5	-	Slater Exchange plus Vosko, Wilk, Nusair Correlation Functional
GGA	-	Generalized Gradient Approximation
PBE	-	Perdew, Burke and Ernzerhof
BP86	-	Becke 1988 Exchange Functional and the Perdew 86 Correlation Functional
LC–wPBE	-	Long Range–Corrected Version of wPBE
CAM–B3LYP	-	Long Range Corrected Version of B3LYP Using the Coulomb–Attenuating Method
B2PLYP	-	Semiempirical Hybrid DFT (Becke (B), Lee, Yang, and Parr (LYP)) with Perturbative Second–Order Correlation
B2PLYPD	-	B2PLYP with Empirical Dispersion
PES	-	Potential Energy Surface
BSSE	-	Basis Set Superposition Error
SE	-	Strain Energy
$E(C_k)_{sp-complex}$	-	Single Point Energy calculations of $C_k$ Cage
$E(nH_2)_{sp-complex}$	-	Single Point Energy calculations of $H_2$
$E(C_k)_{opt}$	-	Fully Optimized Energies of the Isolated Fullerene
$E(H_2)_{opt}$	-	Fully Optimized Energies of the Isolated $H_2$ Molecules
DE	-	Dispersion Energy
BDE	-	Bond Dissociation Energy

ZPE	-	Zero Point Energy Correction
PV	-	Pressure–Volume
$H_{C_k}$	-	Enthalpy of Formation for the Optimized $C_k$
$H_C$	-	Enthalpy of Formation of the Carbon Atom
$TNC_{H_2}$	-	Total Natural Charges on $H_2$

## LIST OF SYMBOLS

Quad BTU	-	Quadrillion BTU (British Thermal Unit)
$C_k$	-	Fullerene
@	-	Is Used to Indicate that Atom(s) or Molecule(s) Listed to the Left of the “@” Symbol Are Encapsulated in the Fullerenes (Right Side)
$nH_2$	-	Number of Hydrogen Molecule
$nH_2@C_k$	-	Endohedral Hydrogen Fullerenes
$\hat{H}$	-	Hamiltonian Operator
E	-	Numerical Value of the Energy
$\Psi$	-	Wavefunction
$\hat{T}$	-	Kinetic Energy Operator
$\hat{V}$	-	Potential Energy Operator
$m_i$	-	Mass of Particle $i$
$e_i$	-	Electric Charge of Particle $i$
$h$	-	Planck’s Constant
$\nabla_i^2$	-	Laplacian Operator
$\Psi^{elec}$	-	Electronic Wavefunction
$\xi$	-	Spin Coordinates
$\alpha(\xi)$ and $\beta(\xi)$	-	Spin Wavefunctions
$\chi(x, y, z, \xi)$	-	Spin orbital Wavefunction
$C_{\mu i}$	-	Coefficients of Linear Combination
$\Psi_i$	-	$i$ –th Molecular Orbital
$\phi_\mu$	-	$\mu$ – th Atomic Orbital
ij or ijk	-	Number of Primitives for Contractions in the Valence Shell

$“+”$	-	Signifies the Diffuse Functions
$“*”$	-	Presence of Polarization Functions
$\Delta E$	-	Complexation Energy
$\varepsilon_0$	-	Vacuum Permittivity
$q_m$	-	Electric Charge of Particle m
$\varepsilon$	-	Relative Expansion of the $C_k$ Cage
$R$	-	Radii of the Expanded Fullerene
$R_0$	-	Radii of the Relaxed Fullerene
$f_{C_k-C_l}$	-	Force Between Two Adjacent C Atoms of Fullerene Cage
$f(nH_2 \cdots C_k)$	-	Total Force Between the Hydrogen Molecule and All C Atoms of the $C_k$ Cage
$U(nH_2 \cdots C_k)$	-	Total Coulomb Energies Between the Hydrogen Molecule(S) and $C_k$ Cage
$r_{kl}$	-	Bond Length of $C_K - C_L$



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## **CHAPTER 1**

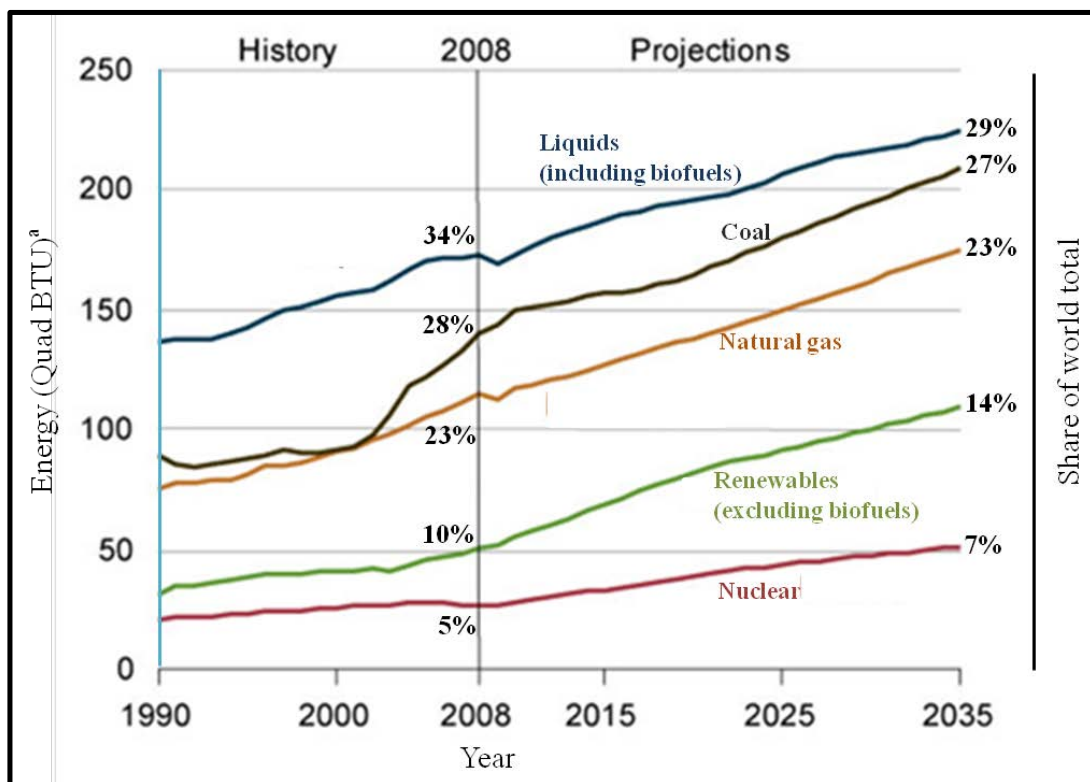
### **INTRODUCTION**

#### **1.1 Overview**

It is well known that, energy is the one of the most important factors in agriculture, manufacturing, mining, transportation, and technology and plays the main role in economic growth. Soon after the industrial revolution in 1750s, fossil fuels (coal, petroleum and natural gas) became the most important energy carrier, and currently we still gain most of our energy from this non-renewable energy sources (Figure1.1). There are two main important reasons that prompt the scientists to find out alternative fossil fuels: First, the rise in world population, which caused the demand for energy and fossil fuel resources to deplete rapidly. Second, the environmental issues which can be attributed to the increase in the consumption of fossil fuels. Examples are greenhouse gas accumulation, climate change, acidification, ozone layer depletion, air pollution, water pollution, oil spills, damage to land surface and etc.

Some famous advanced fuels include biodiesel, bioalcohol, chemically stored electricity, hydrogen, non-fossil methane, non-fossil natural gas, vegetable oil, and other biomass sources. In finding out the alternative energy source, hydrogen is often put at the top list of candidates. It can be produced by reforming natural gas or another fossil fuel, biomass and even by electrolyzing water. Other advantages of hydrogen is that it can be easily produced, suitable fuel for transportation, has ability

to convert easily to other energy forms, high consumption efficiency and environmentally friendly properties (Cheng *et al.*, 2001). Therefore, hydrogen has been recognized as an ideal energy carrier and serves as an ideal energy source to replace fossil fuels.



**Figure 1.1** World energy consumption by fuel, 1990–2035 (<sup>a</sup> Quad BTU =  $1.055 \times 10^{18}$  joules = 1.055 EJ) (U.S. Energy information administration, 2011)

If hydrogen is used in perfect conditions, hydrogen can produce the cleanest form of energy since the only product of its burning is  $H_2O$ . However, to widen its use, developing safe, reliable, compact, and cost-effective hydrogen storage technology is one of the most technically challenging barriers. Ideal hydrogen storage medium (hydrogen carriers) should have high gravimetric and volumetric density, fast kinetics, and favorable thermodynamics. Up to now, there are four major techniques under investigation and in use to store hydrogen. These methods include physical storage via compressed gas or liquefaction, chemical storage in hydrogen carriers (e.g. methanol, ammonia), metal hydrides, and gas-on-solid

adsorption (physical and chemical) (Türker and Erkoç, 2003). Particular interest has been devoted to metal hydrides, nanotubes (Ye *et al.*, 1999), fullerenes, nanofibers (Chambers *et al.*, 1998; Park *et al.*, 1999) and activated carbons (Noh *et al.*, 1987; Hynek *et al.*, 1997; Bénard and Chahine, 2001).

In view of the above arguments, particular attention has been paid to hydrogen containers. Within the current discussion of hydrogen storage, carbon nanostructures as possible alternative for encapsulating hydrogen, such as endohedral fullerenes or nanotubes containing hydrogen molecules are specially promising (Dresselhaus *et al.*, 1996a). In such composites, a fullerene or nanotube plays the role of nanocage whose inner cavity is filled with hydrogen molecules (Monthieux, 2002). After the first theoretical prediction of endohedral fullerenes with a single hydrogen molecule inside  $C_{60}$  fullerene in 1991, as the first idea of storing hydrogen inside a fullerene cage (Cioslowski, 1991), numerous investigations have been carried out on the interaction of  $C_k$  with hydrogen atoms and molecules both experimentally and theoretically (Ren *et al.*, 2006).

Depending on their sizes, fullerenes have limited capacity to encapsulate a certain number of hydrogen molecules. Finding the maximum fullerenes nanocage capacity for hydrogen storage and utilization of fullerenes and carbon nanotubes as hydrogen storage devices are among the hottest research topics nowadays (Dolgonos, 2005; Helena, 2006; Türker and Erkoç, 2006; Dodziuk, 2007; Grygoriy, 2008; Riahi *et al.*, 2009; Dolgonos and Peslherbe, 2011). In this work, the physical and chemical properties of endohedral hydrogen fullerenes and maximum capacity of selected fullerenes to encapsulate hydrogen molecule(s) will be theoretically investigated.

## 1.2 Background of the Problem

According to the definition of a nanomaterial, which was adopted by the European Commission on 18 October 2011 (European Commission, 2011): “A nanomaterial is a natural, incidental or manufactured material containing particles, in

an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm”. There are many types of intentionally produced nanomaterials such as Carbon Based Materials, Metal Based Materials, Dendrimers (Zhang and Hu, 2007; Zhou *et al.*, 2009) and Composites while a variety of others are expected to appear in the near future.

Among the various types of C nanostructures, fullerenes are attractive for possible applications. A fullerene is a molecule which is formed only of carbon atoms, in the form of a hollow sphere or ellipsoid. Spherical fullerenes are also called buckyballs. Carbon nanotube or buckytube is the name of cylindrical ones. From a structural viewpoint, fullerenes are similar to graphite, which is made of graphene sheets of linked hexagonal rings; they can also contain pentagonal or even heptagonal rings.

After the first discovery of C<sub>60</sub> fullerene in 1985 (Kroto *et al.*, 1985), and carbon nanotube by Iijima in 1991 (Iijima, 1991), various carbon-based nanocage structures have been studied for various possible applications. Examples are fullerene clusters (Kratschmer *et al.*, 1990; Diederich and Whetten, 1992; Smalley, 1992; Hunter *et al.*, 1993; Piskoti *et al.*, 1998), single-walled nanotubes (Bethune *et al.*, 1993; Iijima and Ichihashi, 1993), multi-walled nanotubes (Iijima, 1991), nanocapsules (Ruoff *et al.*, 1993; Saito *et al.*, 1993a), nanopolyhedra (Oku *et al.*, 2000), cones (Klaus, 1995; Krishnan *et al.*, 1997), cubes (Saito and Matsumoto, 1998), polyhedral (Ruoff *et al.*, 1993), spheres (Saito *et al.*, 1993b), and carbon onions (Ugarte, 1992).

Fullerenes as hollow clusters are one of the intriguing nanocage structures that can be used in medicine (Cagle *et al.*, 1999; Bakry R, 2007; Bolskar, 2008), in photovoltaic devices (Ross *et al.*, 2009; Clarke and Durrant, 2010), and in electronics (Kobayashi *et al.*, 2003; Shibata *et al.*, 2004), and in particular as single-molecule transistors for quantum computing (Meyer *et al.*, 2002; Twamley, 2003; Garelli and Kusmartsev, 2005). Of special interest are the so-called peapods formed by carbon

nanotubes filled with endohedral fullerene complexes such as N@C<sub>60</sub> (Twamley, 2003) or P@C<sub>60</sub> (Whitener *et al.*, 2008) which are considered as promising elements of quantum-processing architecture (Korona and Dodziuk, 2011).

Among the various interesting properties of fullerenes, the possibility to synthesize endohedral fullerenes including different atoms and molecules is attractive for various possible applications (Dresselhaus *et al.*, 1996a). In such compounds, a fullerene or nanotube plays the role of nanocage whose inside cavity is filled with foreign atoms or molecules (Monthieux, 2002). In particular, the possibility of filling a fullerene cage with atomic, ionic, or molecular guests was proposed rapidly after the discovery of C<sub>60</sub>.

The first theoretically prediction of endohedral fullerenes with a hydrogen molecule inside by Cioslowski in 1991 (Cioslowski, 1991) was an intriguing challenge to synthesize endohedral fullerenes. Experimentally, using "molecular surgery" approach, endohedral C<sub>60</sub> fullerene containing one H<sub>2</sub> molecule and C<sub>70</sub> fullerene containing one and two H<sub>2</sub> molecules can be synthesized. To produce H<sub>2</sub>@C<sub>60</sub> and H<sub>2</sub>@C<sub>70</sub> using this method, a series of organic reactions is needed, where an orifice is opened in the fullerene cage and H<sub>2</sub> molecule is inserted through the orifice, which is then closed leaving H<sub>2</sub> trapped inside (Rubin *et al.*, 2001; Murata *et al.*, 2003; Komatsu *et al.*, 2005; Murata *et al.*, 2008c).

During the last two decades, calculations based on molecular mechanics, semiempirical, or density functional theory (DFT) have been carried out in order to investigate the stability and properties of endohedral fullerenes, in particular endohedral C<sub>60</sub> and C<sub>70</sub> fullerenes encapsulating H<sub>2</sub> molecule(s). One of the most important issues in hydrogen-filled fullerene molecules is that, how many hydrogen molecules can be encapsulated in fullerene cage?

Nevertheless, there is still an increasing debate on the number of hydrogen molecules encapsulated inside the fullerene C<sub>60</sub>, where, for example, some groups predicted a number of up to 29 molecules of H<sub>2</sub> that can be encapsulated inside C<sub>60</sub>

(Barajas–Barraza and Guirado–López, 2002; Türker and Erkoç, 2003; Koi and Oku, 2004; Türker and Erkoç, 2006; Chih–Kai, 2007; Pupysheva *et al.*, 2007; Soullard *et al.*, 2008). This number is far from experimental realization, to the best of our knowledge.

### 1.3 The Problem Statement

Two most important problems have been reported by researchers when investigating endohedral complexes of fullerenes with hydrogen molecules. First, the height of the energy barrier estimation for insertion a guest inside the fullerene cage, and second, the capacity limit of H<sub>2</sub> molecules that can be encapsulated. The issue of the energy barrier estimation, which will not be discussed here, especially for the hydrogen molecule entering the C<sub>60</sub> fullerene cage has been reported in several papers (Koi and Oku, 2004; Seifert, 2004; Ramachandran *et al.*, 2008). The second important issue in hydrogen–filled fullerene molecules is that, how many hydrogen molecules can be encapsulated inside a fullerene cage.

The stability of complexes of hydrogen molecule(s) encapsulated inside the C<sub>60</sub> cage has been studied by various approaches, from molecular mechanics (MM), through semiempirical and density–functional theory (DFT), to *ab initio* quantum chemical methods (Korona *et al.*, 2009). Finding the fullerene nanocage capacity for hydrogen storage is the challenge of the most of these reports and the results appear contradictory. Indeed, there is no agreement on the amount of hydrogen encapsulated inside a C<sub>60</sub> fullerene. On the one hand, one group stated that there is not enough space for more than one hydrogen molecule that can be encapsulated inside C<sub>60</sub> while, on the other hand, the other group claimed that theoretically C<sub>60</sub> can encapsulate more than one hydrogen molecule (see literature review, Table 2.3).

By means of theoretical methods these two groups have calculated the formation energy of nH<sub>2</sub>@C<sub>60</sub> complexes. However, while the first group have concluded that only H<sub>2</sub>@C<sub>60</sub> complex is stable based on some general geometric

considerations, particularly van der Waals radius of an H and  $sp^2$  hybridization of the carbon atom, the second group using only the calculation results, have concluded that more than one hydrogen molecule can be encapsulated inside the  $C_{60}$  (see literature review, Table 2.3).

To the best of our knowledge, the two groups have neglected several important physical and chemical properties of fullerenes such as charge transfer, coulomb energy, bond dissociation energy, C–C coulomb force, and strain and dispersion energies.

In this study, by means of *ab initio* calculations, we are going to investigate the geometrical parameters and energies of a series of selected isolated fullerenes (such as  $C_{60}$  and  $C_{70}$ ) as well as their corresponding endohedral hydrogen fullerenes ( $nH_2@C_k$ ) and finally, we will provide the capacity limit of the  $H_2$  molecule encapsulated fullerenes, based on the above mentioned criteria.

#### **1.4 Purpose of the Research**

The purpose of this research is to investigate the physical and chemical properties of  $H_2$  molecule encapsulated inside  $C_k$  ( $k \geq 50$ ) by means of theoretical methods. This includes the complexation energies, geometrical structures, host–guest interactions, cage expansion and bond dissociation energy that have been ignored in the previous works. We also aim to provide the capacity limit of  $H_2$  molecule encapsulated inside the selected fullerenes. The third purpose is to figure out the theoretical method (or methods) appropriate to such problems.

#### **1.5 Objective of the Research**

Owing to the lack of information on the physical and chemical properties stated above, the aims of this research are:



- i. To investigate the geometrical parameters and energies of a series of selected isolated fullerenes ( $C_{50}$ ,  $C_{60}$ ,  $C_{70}$  and  $C_{78}$ ) as well as their corresponding endohedral hydrogen fullerenes ( $nH_2@C_k$ ,  $k = 50, 60, 70$  and  $78$ ) upon encapsulation of one or more  $H_2$  molecule by means of theoretical methods.
- ii. To find out the capacity limit of the  $H_2$  molecule encapsulated inside selected fullerenes.
- iii. To figure out the most appropriate method(s) that give(s) reasonable and acceptable answers for the encapsulation of  $H_2$  molecule inside fullerene and, which agree(s) with the experimental findings (when available).

## 1.6 Significance of Research

According to the introduction, clean hydrogen energy is an important fuel and carbon nanostructures always play a major role in contemporary discussions of hydrogen storage media. In such composites, endohedral  $C_k$  fullerene containing hydrogen molecule ( $H_2@C_k$ ) has become an attractive species for these purposes.

Nevertheless, the findings of this research will help the scientists to choose the appropriate fullerene as well as monitoring the mechanism to produce an endohedral fullerene with higher hydrogen storage. In view of the above, the significance of this research can be summarized in the followings:

- i. To provide guidance to theoretical scientists to choose the most appropriate theoretical method for investigating endohedral fullerenes.
- ii. To provide guidance to experimental scientists to choose the suitable fullerene(s) for encapsulating hydrogen inside the cage(s).
- iii. To avoid the trial-and-error in experiments.

## 1.7 Scope of the Research

$C_{60}$  molecule, in view of its technological availability, is the most abundant and most stable form of fullerenes. For this reason, over the last two decades, it has been chosen by researchers as a model to conduct studies on the physical and chemical properties of this type of materials. Recently  $C_{70}$  and a few other higher fullerenes were also used.

In this research, by means of theoretical methods we investigated the physical and chemical properties of a series of isolated fullerenes ( $C_{50}$ ,  $C_{60}$ ,  $C_{70}$ , and  $C_{78}$ ) as well as their corresponding endohedral hydrogen fullerenes ( $nH_2@C_k$ ,  $k = 50, 60, 70$  and  $78$ ). For each fullerene we provided the capacity limit of  $H_2$  molecule encapsulation.

## 1.8 Organization of this Thesis

In this thesis, *ab initio* molecular orbital (MO), density functional theory (DFT) and double-hybrid density functionals comparative studies of fullerene nanocage capacity for hydrogen storage have been carried out. This thesis is organized as follows. In chapter two, literatures on previous works on endohedral fullerenes are reviewed. Chapter three is broadly divided into two parts. The first part deals with the theoretical methods. The quantum theory related to molecular mechanics, semi-empirical methods and *ab initio* quantum chemistry are highlighted. The second part describes in detail the simulation methodology, including the complexation energy, geometrical parameters, cage expansion, coulomb energy, strain energy, dispersion energy and bond dissociation energy. Results of *ab initio* MO and DFT calculations for endohedral hydrogen fullerenes ( $nH_2@C_k$ ,  $k = 50, 60, 70$  and  $78$ ) and analysis of results are presented in chapter four. Finally, chapter five concludes this thesis.

In the case of endohedral hydrogen fullerenes, whose stability is mainly due to London dispersion interactions, the situation is much more complicated. Semiempirical methods are known to give unreliable results. Furthermore, it was found that the several DFT functionals tend to underestimate the stabilization energy in endohedral hydrogen fullerenes while MP2 method tend to overestimate it. Most importantly, the more sophisticated and computationally demanding quantum chemistry methods that take into account electron correlation are still impractical in fullerene research since their scaling of computational cost with respect to basis set size is too steep.

#### **5.4 Direction of Future Researches**

Many aspects of the physics and chemistry of fullerenes are understood by now but many others still constitute an open question. An example of this is the subject of this study. Indeed, determination of the number of hydrogen molecules that can be hosted by a fullerene  $C_k$  cage continues to be debatable. In view of the results presented in this thesis, the proposed future works can be summarized in the following:

- i. Extend the study to other fullerenes by using theoretical methods.
- ii. Find out the appropriate theoretical method or methods that can handle such problems.
- iii. Carry out experiments on the theoretically predicted endohedral hydrogen fullerenes.

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Tb<sub>3</sub>N@C<sub>88</sub> and Tb<sub>3</sub>N@C<sub>86</sub> as well as the  $I_h$  and  $D_{5h}$  Isomers of Tb<sub>3</sub>N@C<sub>80</sub>.  
*Journal of the American Chemical Society*. 129(7), 2035–2043.